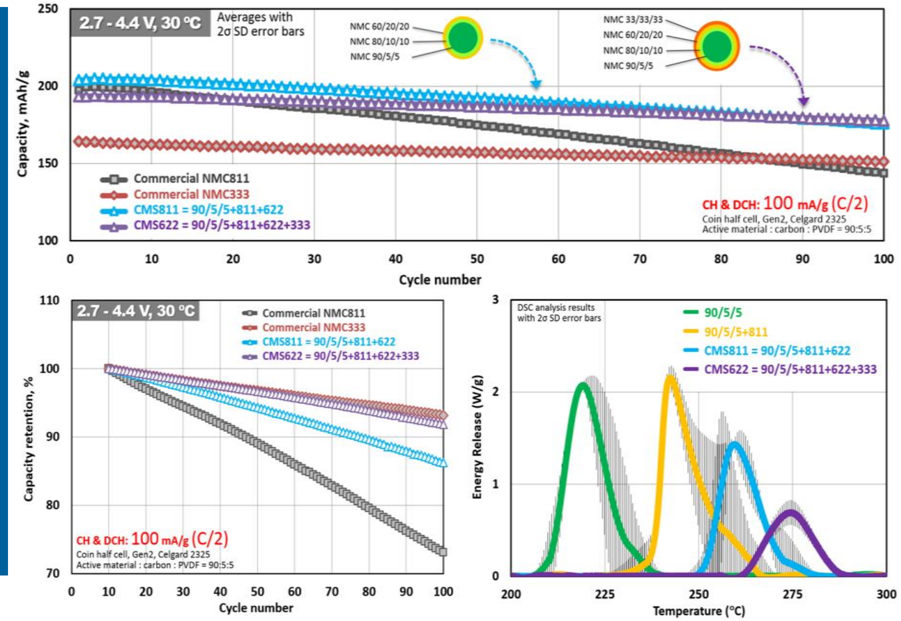
Process Development and Scale-up of Advanced Active Battery Materials – Gradient Cathode Materials



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Argonne National Laboratory

Project ID: BAT167

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Arlington, Virginia

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Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2018
- Percent complete: on going

Budget

- Total project funding:
  - $1.1M in FY17
  - $1.2M in FY18

    $500K for Hydro/Solvothermal System

Barriers

- Cost: Reduce manufacturing costs with advanced, continuous processing methods
- Performance: Optimization of particle structure and composition combination for maximum performance of gradient material

Partners

- Active material process R&D:
  - University of Wisconsin
    - Particle strength analysis
  - Argonne's CAMP
    - Coin full cell evaluation
    - Pouch cell evaluation
  - Brookhaven National Laboratory
    - FIB for electron microscopy
    - XANES and EXAFS
    - Hard X-ray nanoprobe imaging
    - Thermal stability studies
  - Laminar
    - Development and scale-up of Taylor Vortex Reactor process

Objectives - Relevance

- The objective of this program is to carry out a systematic research to:
  - Synthesize and evaluate various types of concentrated gradient cathode materials to improve ***thermal stability*** and suppress ***impedance rise***.
  - Develop cost-effective ***batch and continuous processes*** for concentrated gradient cathode materials.
  - Provide ***sufficient quantities*** of these materials for pouch cell testing and further industrial validation.

- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing.
    - Reducing the risk associated with the commercialization of new battery materials.
  - This program provides large quantities of materials with consistent quality.
    - For industrial evaluation in large format prototype cells.
    - To support basic research.

Milestones

Year	Category	Milestone	Status	Quarter
2017	*Analysis*	622 Core-Gradient material (NMC811 + 442) – Hard X-ray nanoprobe imaging, Thermal stability (oxygen release)	***Completed***	Q4
	Analysis	811 Core-Shell & Core-Gradient materials (NMC90/5/5 + 333) – DSC, Thermal stability (oxygen release)	***Completed***	
	Process	Process design for hydro/solvothermal synthesis system	***Completed***	
2018	*Synthesis*	100 gram 811 Core-Shell (NMC90/5/5 + 333)	***Completed***	Q1
	Synthesis	100 gram 811 Core-Gradient (NMC90/5/5 + 333)	***Completed***	
	Synthesis	NMC90/5/5	***Completed***	
	Synthesis	Core-Multi Shell NMC90/5/5 + 811	***Completed***	
	Synthesis	100 gram Core-Multi Shell 811 (NMC90/5/5 + 811 + 622)	***Completed***	
	Synthesis	100 gram Core-Multi Shell 622 (NMC90/5/5 + 811 + 622 + 333)	***Completed***	
	Analysis	Characterization, coin cell, DSC and impedance test of Core-Multi Shell materials	***Completed***	Q2
	Analysis	Pouch cell evaluation	Ongoing	
	Synthesis	Co-free lithium-manganese-rich material (Core-Shell & Multi-Band particle structure)	***Completed***	
	Process	Process R&D and patent application for continuous synthesis of gradient materials	Ongoing	
	Analysis	XANES, EXAFS and imaging of Core-Multi Shell materials	Planned	Q3
	Synthesis	Kilogram production of a Core-Multi Shell material	Planned	
	Process	Installation completion of hydro/solvothermal synthesis system	Planned	

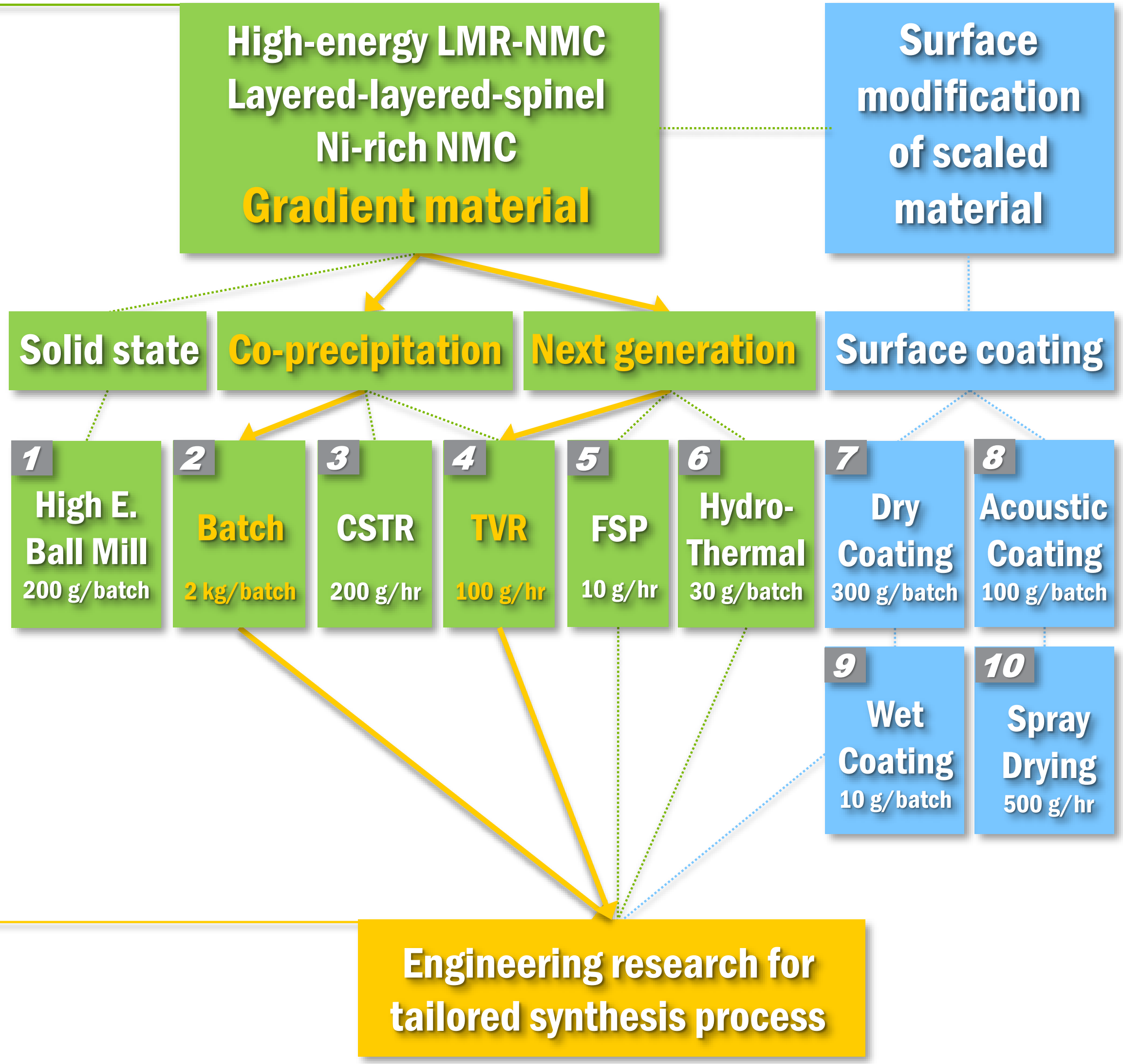
Approach - Strategy

Material Synthesis with Process R&D

- ❑ Define target active material
  - NMC811 and NMC622 gradient materials
- ❑ Select synthesis process and synthesis route
  - Batch and TVR
  - Hydroxide co-precipitation
- ❑ Produce intermediate material
  - Particle morphology and composition design
  - 10 gram preliminary synthesis for coin cell
  - 100 gram synthesis for pouch cell
  - Go/No-Go decision
- ❑ Synthesis process improvement & optimization
- ❑ Production and distribution
  - Kilogram production
  - Baseline material for fundamental research

Emerging Manufacturing Technologies

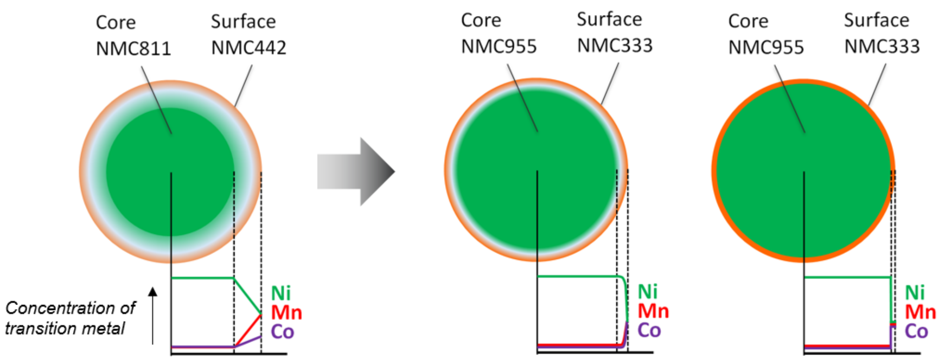
- ❑ Taylor Vortex Reactor
- ❑ Flame spray pyrolysis
- ❑ Hydro/solvothermal synthesis



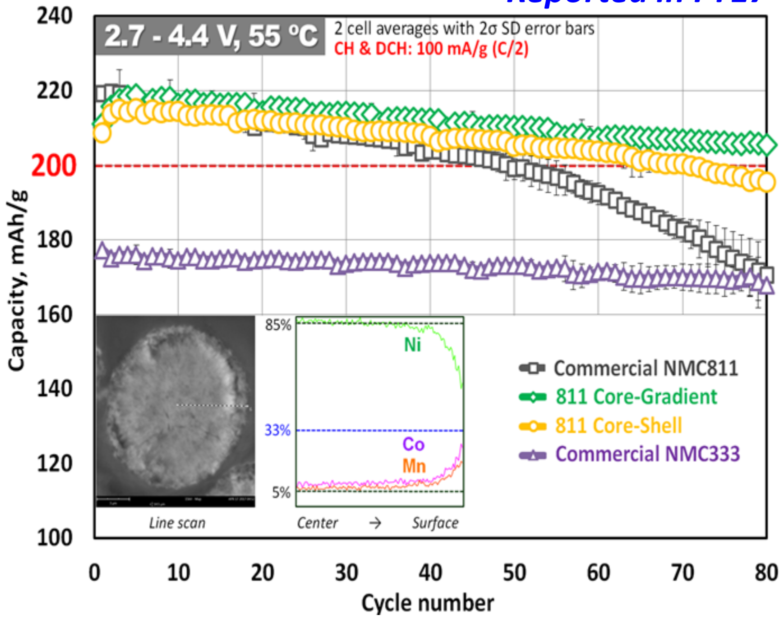
Gradient Material

- For best of core and surface compositions
  - Core: Ni-rich for high capacity
  - Surface: Mn-rich for high stability

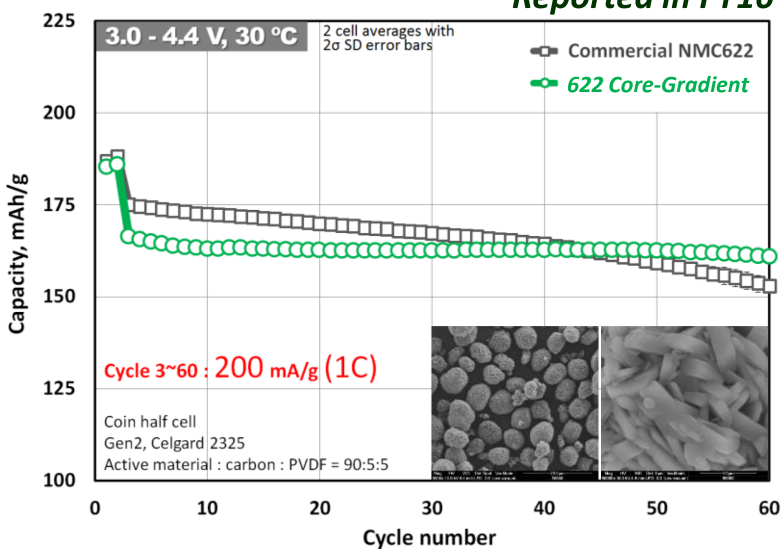
622 Core-Gradient (FY16) **811 Core-Gradient & 811 Core-Shell (FY17)**

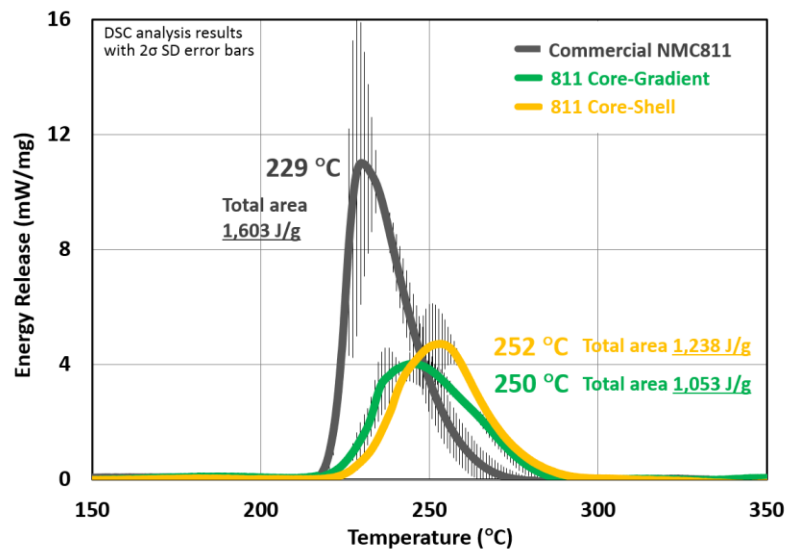


Reported in FY17



Reported in FY16





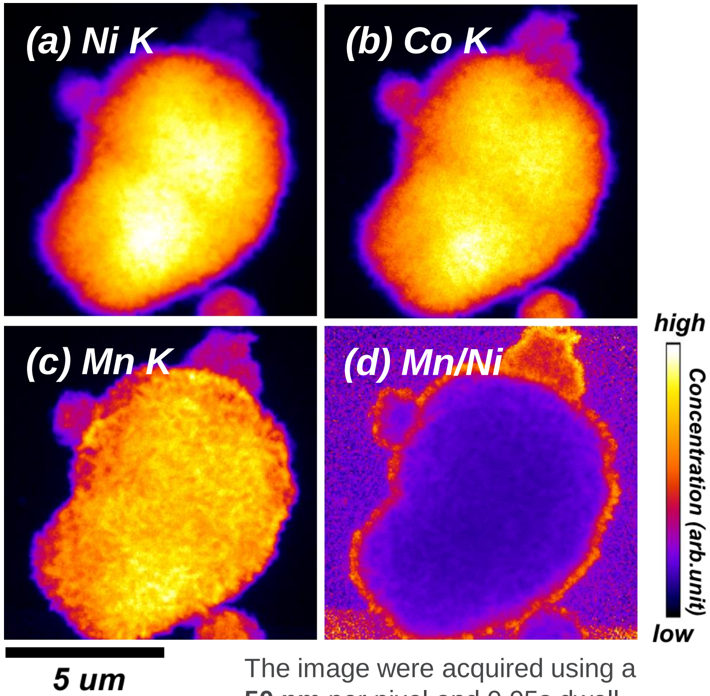
622 Core-Gradient Material Studies

BROOKHAVEN NATIONAL LABORATORY

BAT 059

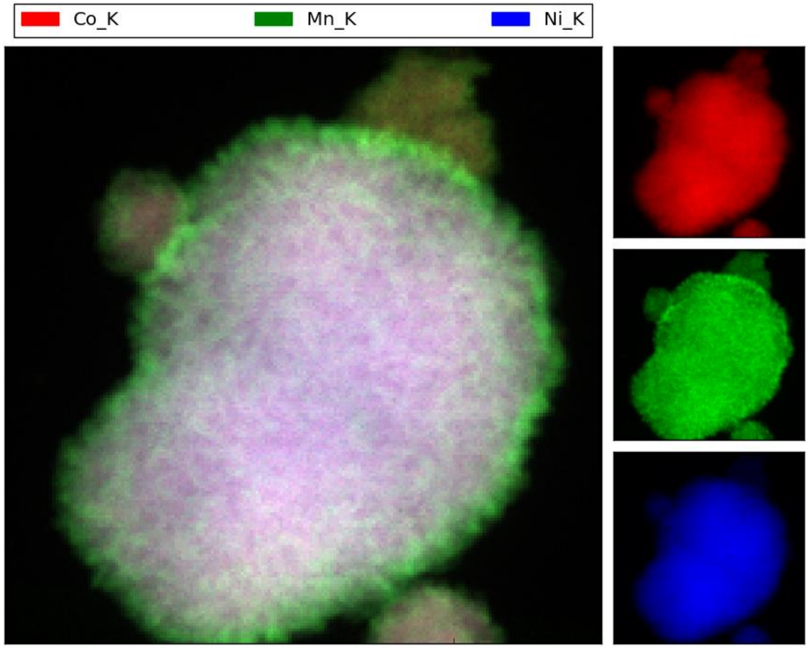
- Hard X-ray Nanoprobe imaging for 622 Core-Shell material
  (Seongmin Bak @ BNL, EES, Dr. Xiao-Qing Yang's group)

X-ray fluorescence image for pristine 622 Core-Gradient



The image were acquired using a **50 nm** per pixel and 0.05s dwell time per pixel (200 x 200 pixels)

Elemental mapping of pristine 622 Core-Gradient



✓ *Elemental specific XRF image confirmed concentration gradient structure in pristine 622 Core-Gradient sample.*

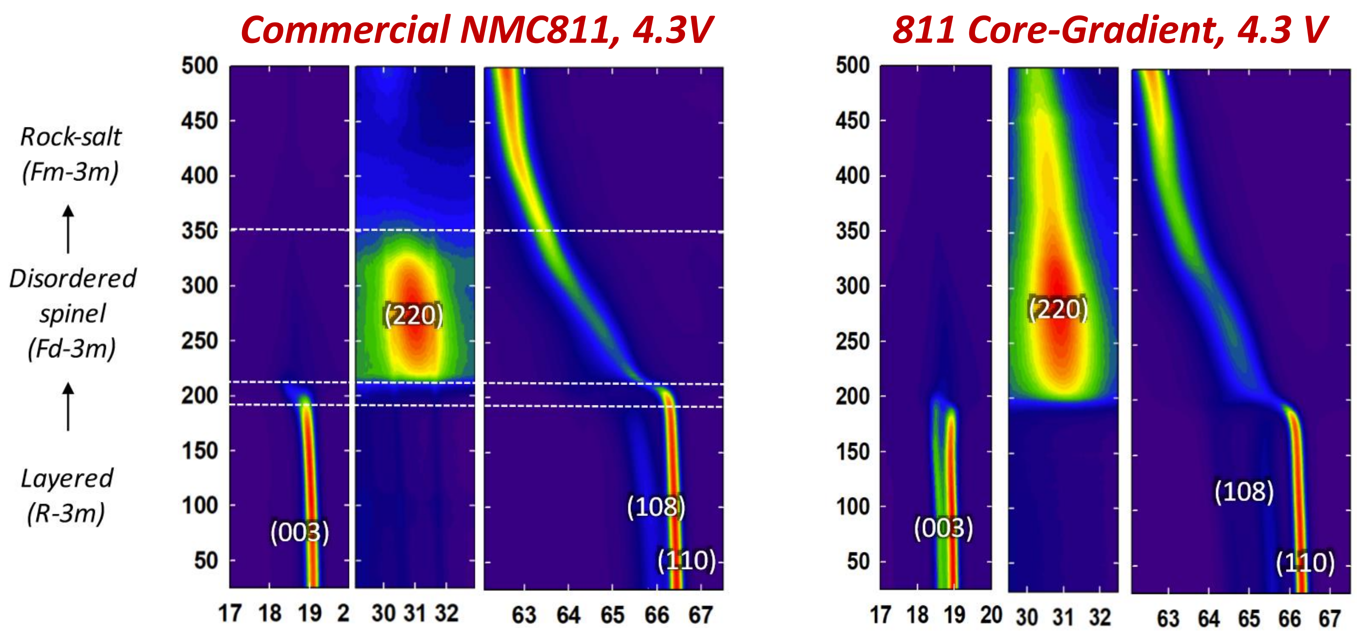
✓ *Imaging for 811 Core-Gradient material is planned*

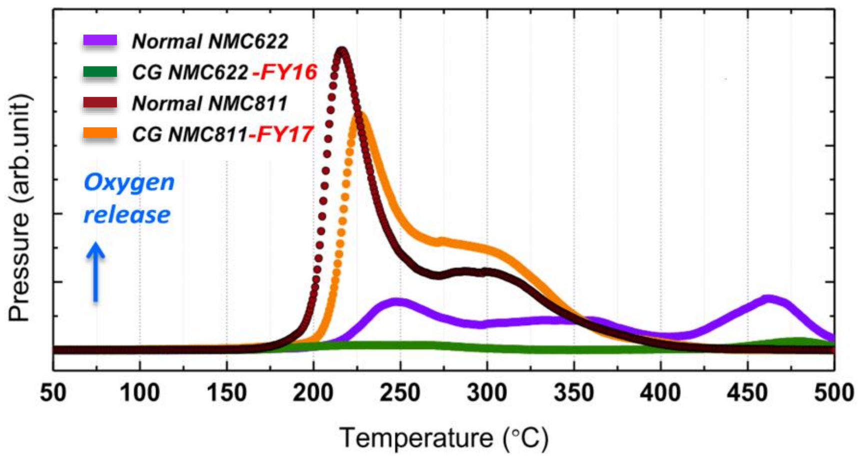
811 Core-Gradient Material Studies

BROOKHAVEN NATIONAL LABORATORY

BAT 367

- Thermal stability of the charged CG NMC811 using time resolved XRD
  (Seongmin Bak @ BNL, EES, Dr. Xiao-Qing Yang's group)

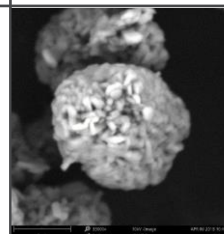
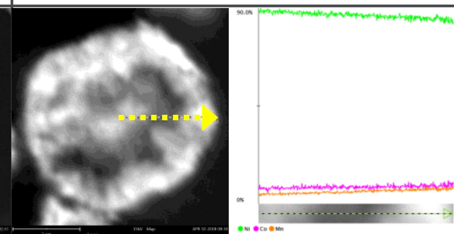
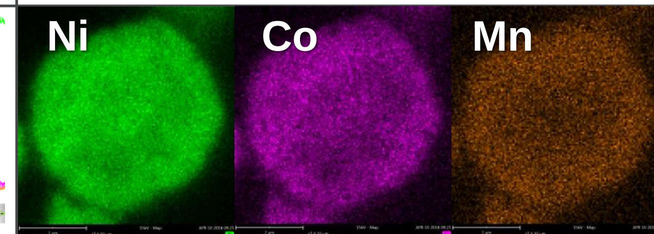
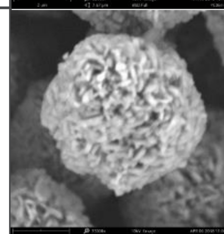
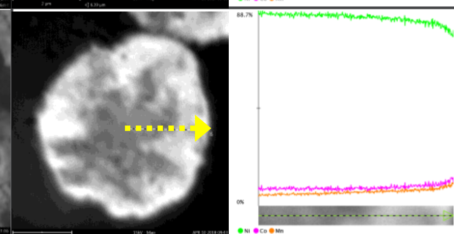
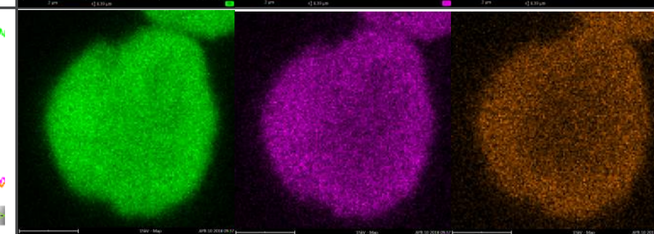
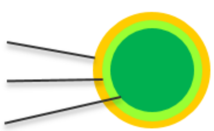
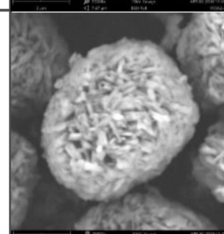
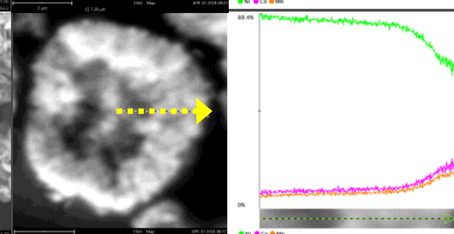
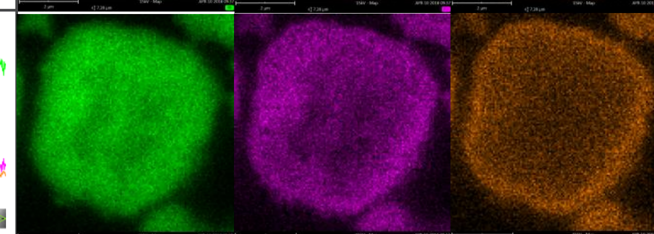
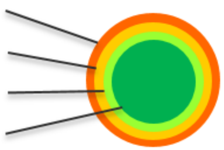
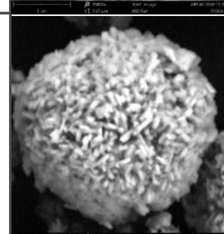
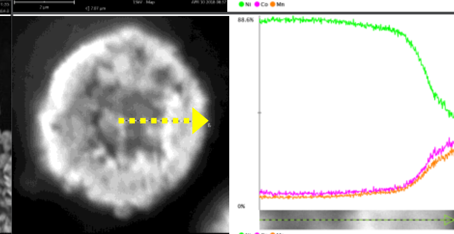
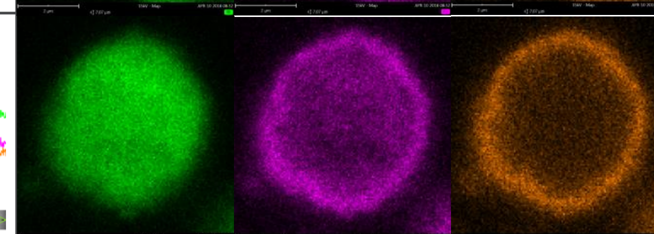




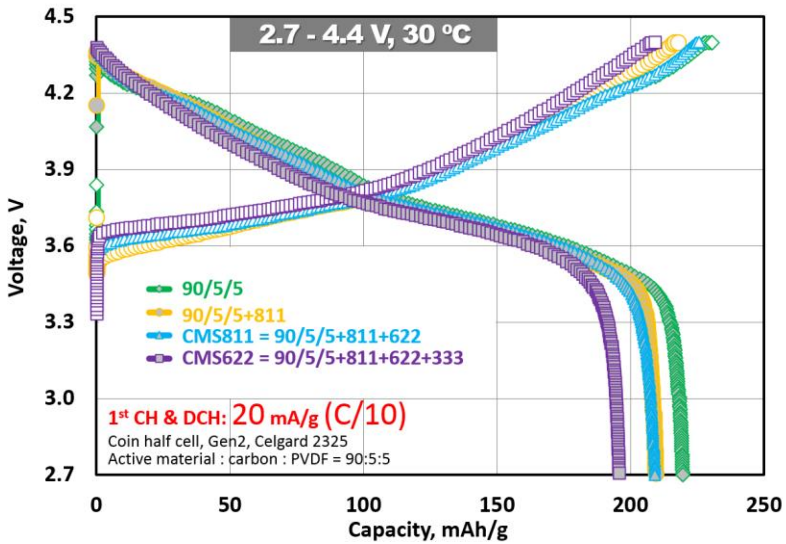
- ✓ *The peak broadening of 811 Core-Gradient indicates more structural inhomogeneity.*
- ✓ *Oxygen release of 811 Core-Gradient started from higher temperature compared to normal NMC811.*
- ✓ *811 Core-Gradient shows improved thermal stability which is a good match to the previous DSC result.*

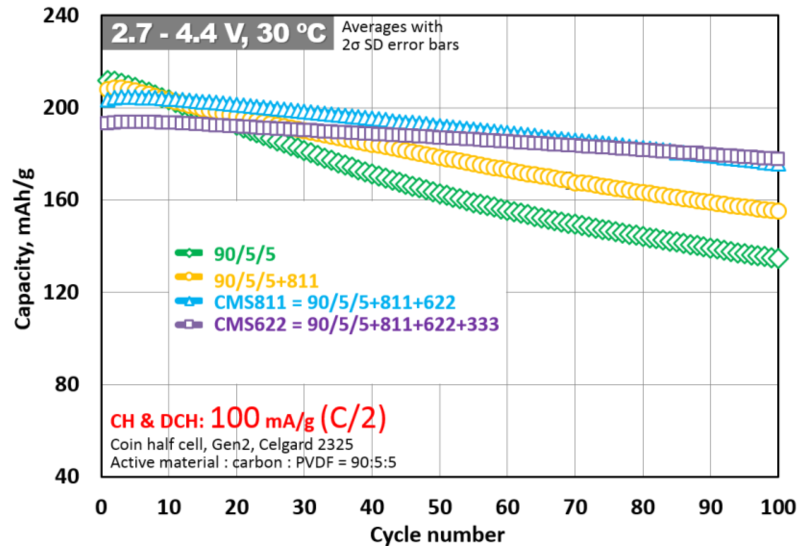
Core-Multi Shell Material

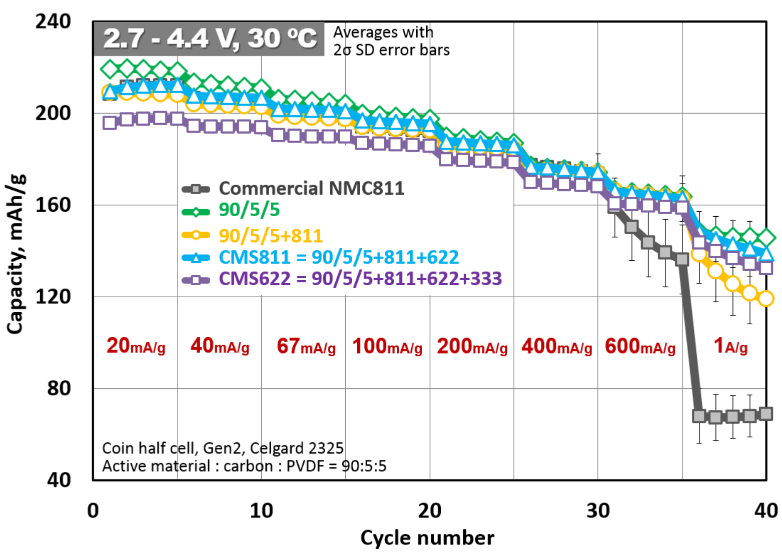
- New synthesis approach toward Core-Multi Shell particle structure

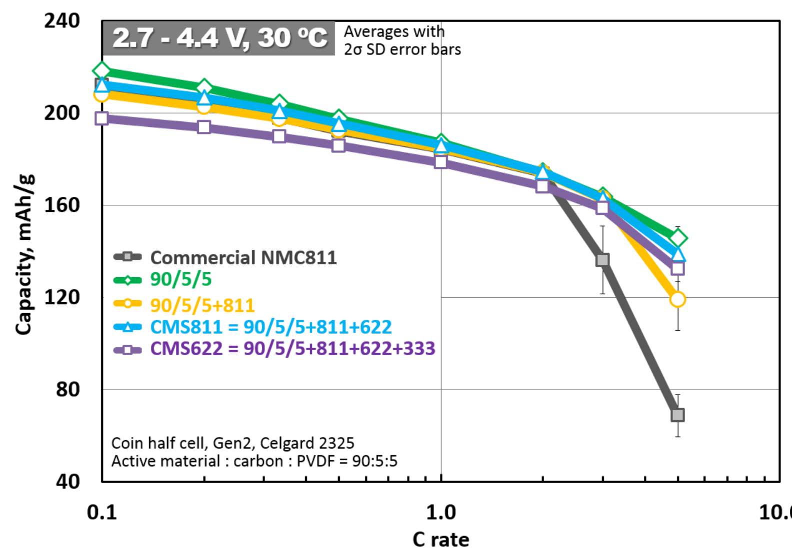
	Core-Multi Shell particle design	SEM	Cross-sectional line scan	Cross-sectional mapping
Ni 90%	 ICP: $Li_{1.0}Ni_{0.90}Co_{0.05}Mn_{0.05}O_2$			
Ni 86%	 ICP: $Li_{1.0}Ni_{0.86}Co_{0.07}Mn_{0.07}O_2$			
Ni 80%	 ICP: $Li_{1.0}Ni_{0.80}Co_{0.10}Mn_{0.10}O_2$			
Ni 63%	 ICP: $Li_{1.07}Ni_{0.63}Co_{0.18}Mn_{0.19}O_2$			

Core-Multi Shell Material





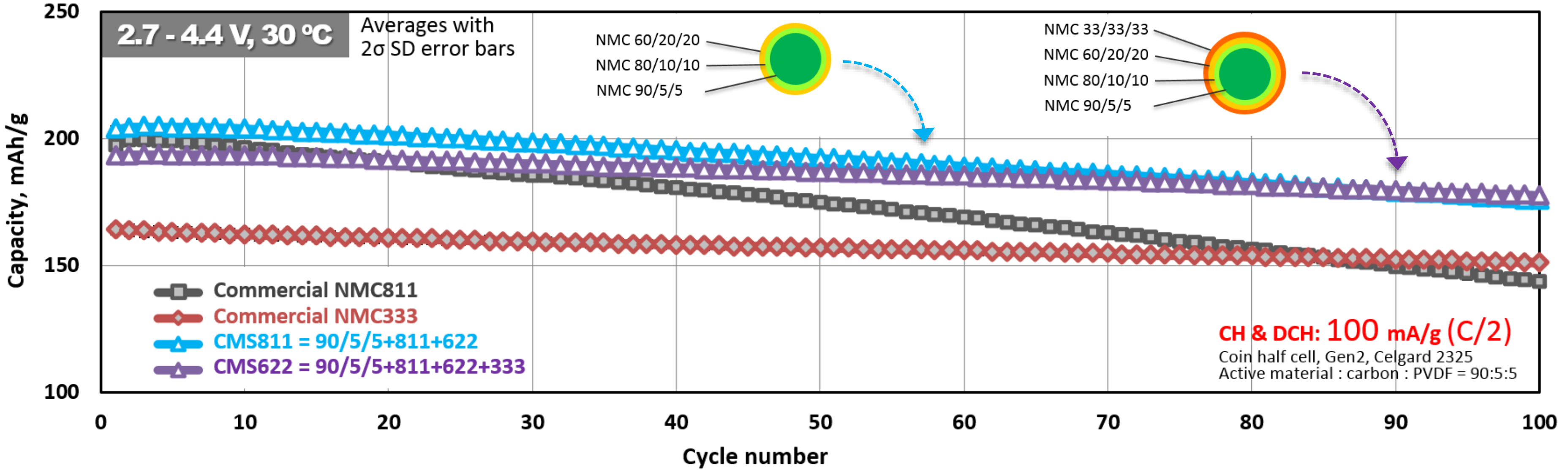


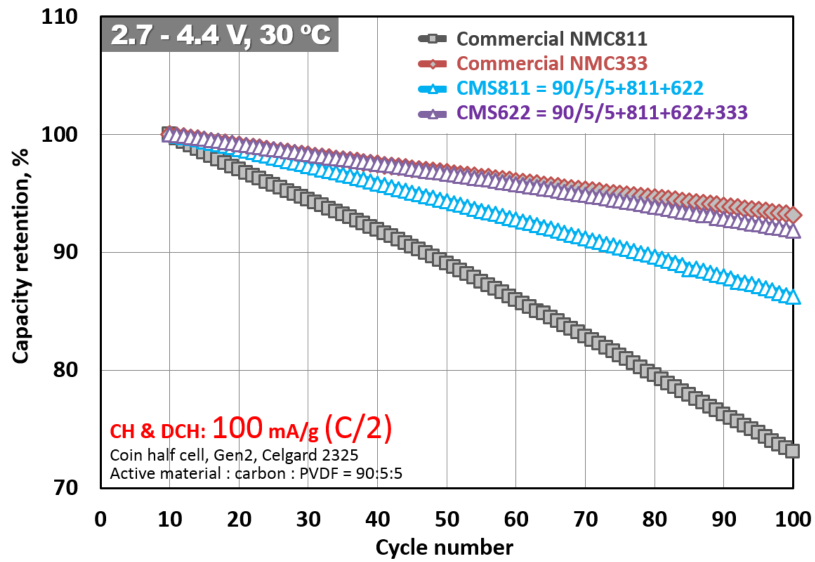


✓ *Core-Multi Shell materials show improved rate capability compared to the commercial NMC811.*

Core-Multi Shell Material

❑ Cycling comparison between CMSs and commercial NMCs



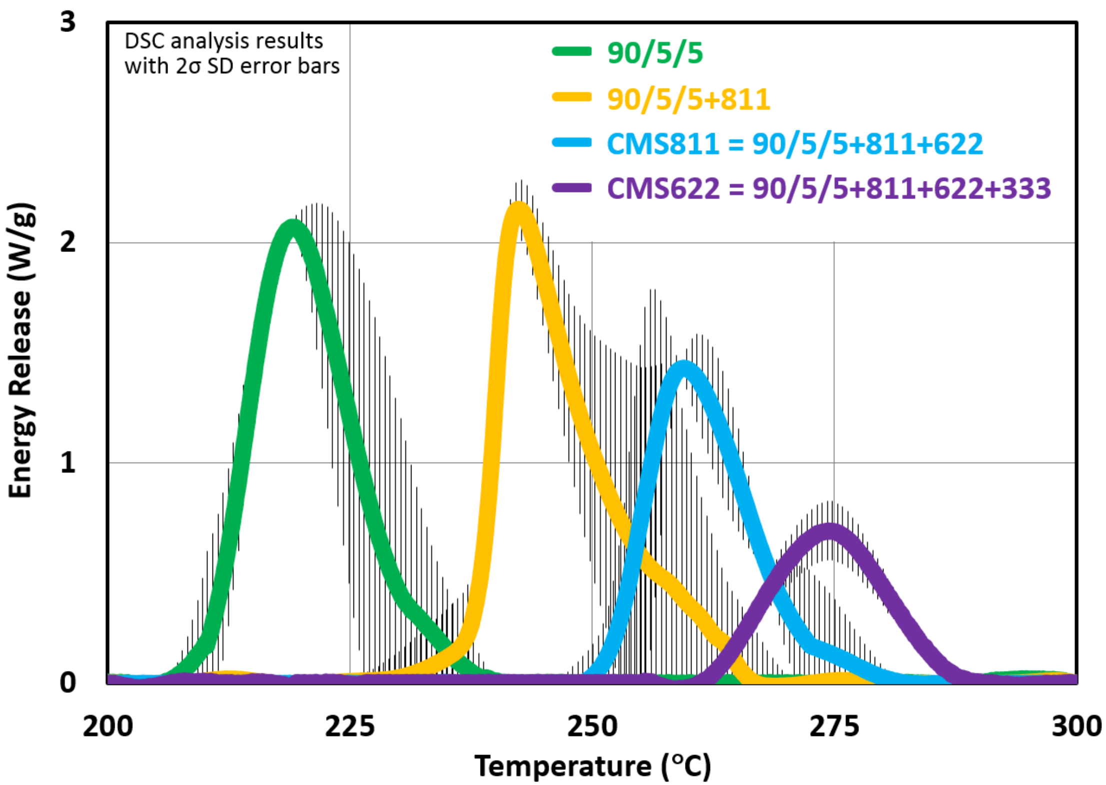


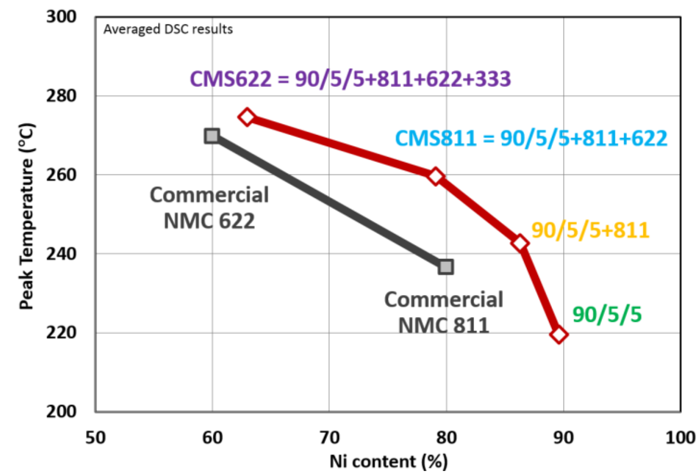
* The material synthesis was tuned based on the performance evaluation of coin half cell at MERF.
(Cathode laminate thickness: 34µm, porosity: 43%)

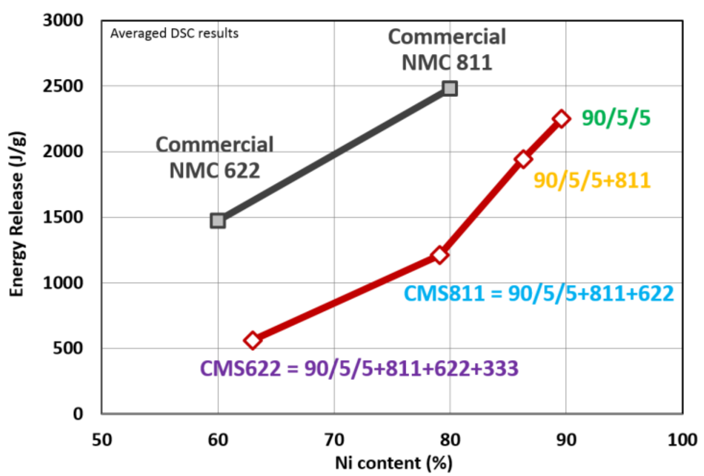
- ✓ *CMS811 and CMS622 show an improved capacity retention compared to Commercial NMC811.*
- ✓ *The capacity retention trends of CMS622 and commercial NMC333 having the same surface composition are similar.*
- ✓ *We are working with CAMP to evaluate the performance of synthesized gradient materials using pouch cells.*

Core-Multi Shell Material

- DSC comparison at 5 C/min rate





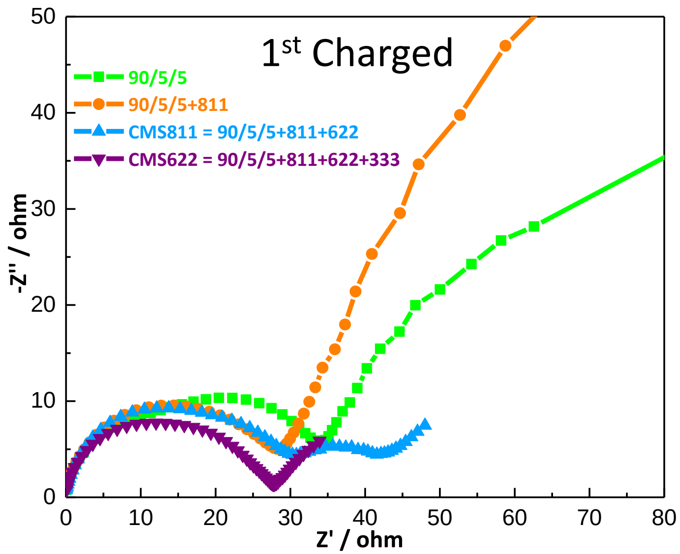


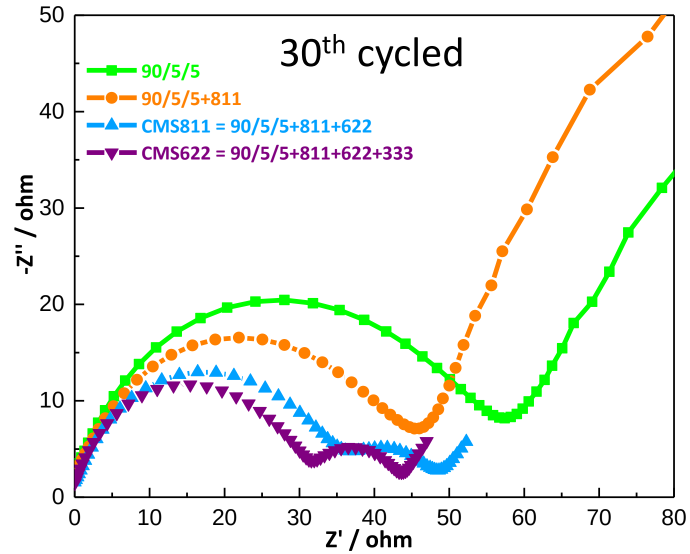
- ✓ *CMS622 exhibits a similar peak temperature compared to the commercial NMC622, but with a 60% reduced energy release.*
- ✓ *CMS811 shows 50% less energy release than commercial NMC811.*
- ✓ *Core-Multi Shell materials show improved thermal stability.*

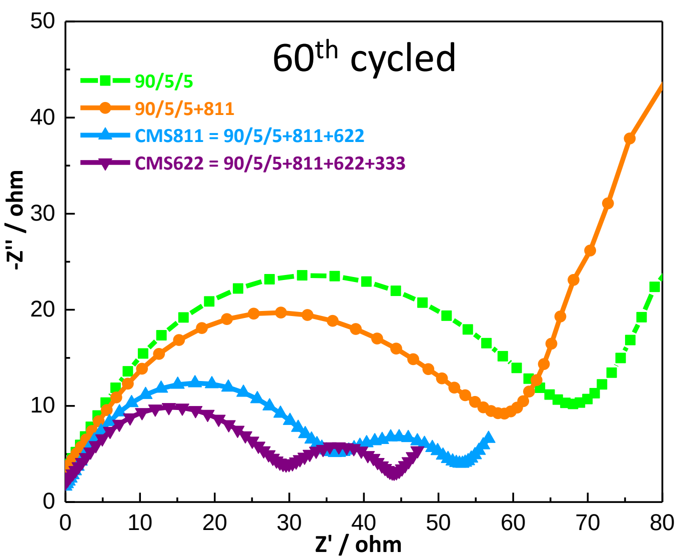
Technical Accomplishments

Core-Multi Shell Material

- ❑ Impedance analysis of CMS materials







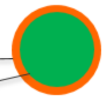
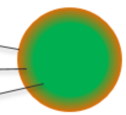
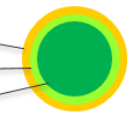
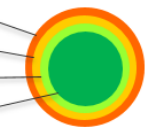
✓ *The higher the cobalt concentration on the particle surface, the more the impedance rise is suppressed.*

✓ *Low impedance growth means longer cycle life.*

Technical Accomplishments

Full Cell Evaluation of Gradient Materials at CAMP

BAT 028

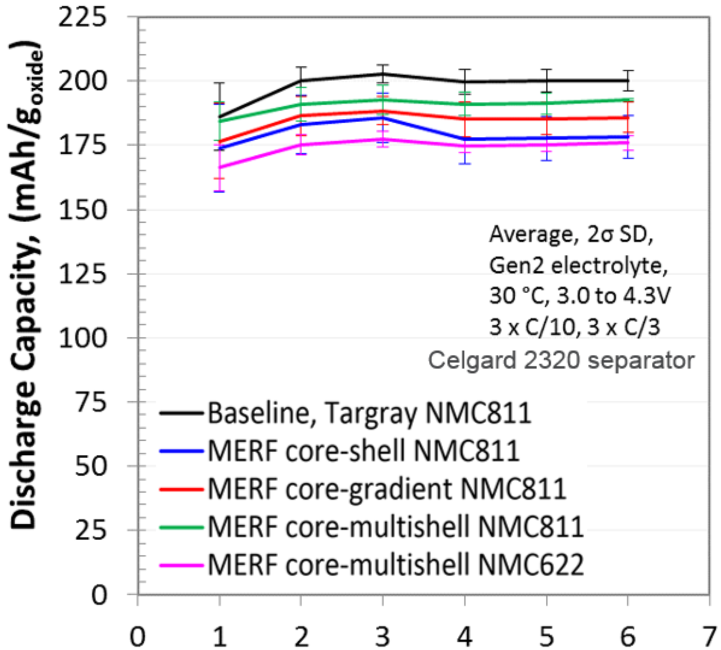
Species	*811 Core-Shell*	*811 Core-Gradient*	*Core-Multi Shell 811*	*Core-Multi Shell 622*
Particle structure	NMC 33/33/33 NMC 90/5/5 	NMC 33/33/33 Gradient layer NMC 90/5/5 	NMC 60/20/20 NMC 80/10/10 NMC 90/5/5 	NMC 33/33/33 NMC 60/20/20 NMC 80/10/10 NMC 90/5/5 
Preliminary synthesis	✓	✓		
Coin full cell test @CAMP	✓	✓		
100 gram Scale-up	✓	✓	✓	✓
Coin full cell test @CAMP	✓	✓	✓	✓
Pouch cell test @CAMP	✓	✓	✓	✓
GO/NO-GO decision	Ongoing			
Kilogram production	Will be determined based on pouch cell evaluation			

✓ *See BAT028 for more details on coin full cell evaluation of 811 Core-Gradient material.*

Full Cell Evaluation of Gradient Materials at CAMP

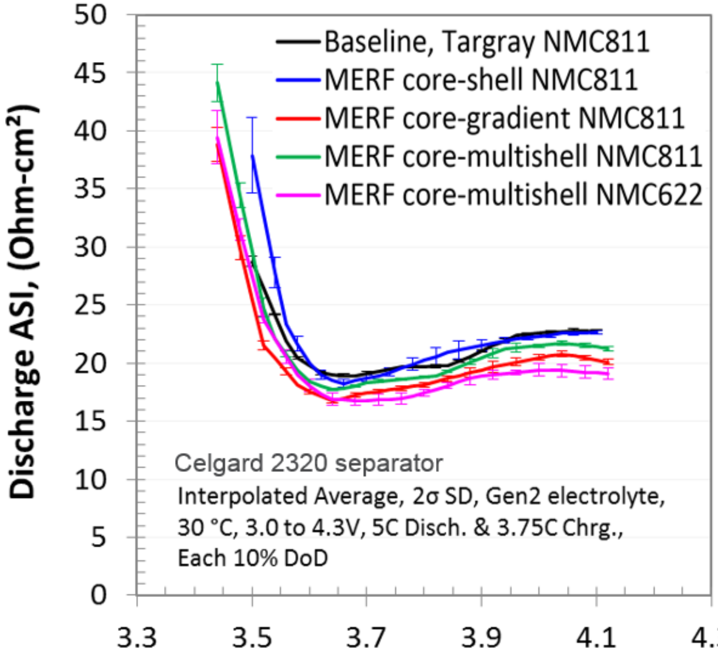
BAT 030

- Formation, Gr//NMC, Single layer pouch cells (~20 mAh)



Formation Protocol:
3.0 to 4.3V
Tap charge to 1.5V, 1.5V hold 15 minutes, rest 12 hours,
3x at C/10, 3x at C/3

- Initial HPPC, Gr//NMC, Single layer pouch cells (~20 mAh)



HPPC Protocol:
3.0 to 4.3V
Charge to 4.3V @ 1C, discharge 10% capacity intervals @ 1C, rest 1 hour, 5C discharge pulse for 10 s, rest 40 s, 3.75C pulse for 10 s

✓ *Initial capacity of gradient materials are lower, but their ASIs are better though they are the first attempted electrodes.*

✓ *We are collaborating with ANL CAMP to improve the material synthesis and pouch cell performance.*

- Gelling issue during electrode making step
- Coin cell vs. pouch cell performance evaluation

✓ *See BAT030 for more details on pouch cell evaluation of Gradient materials.*

Cobalt-free Lithium-manganese-rich Material

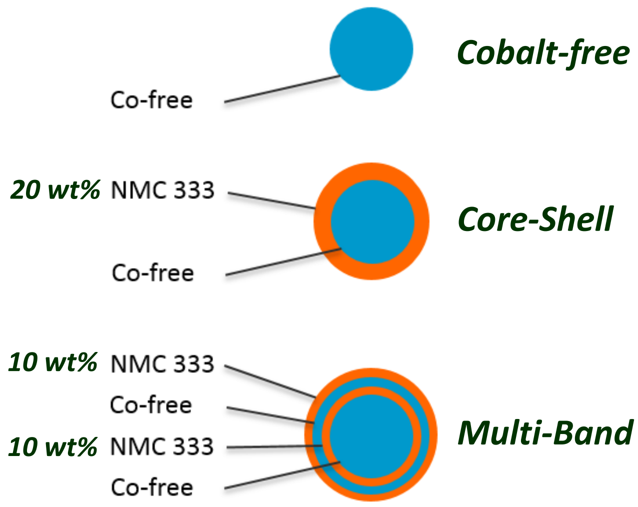
Cobalt plays an important role in stabilizing the structure and positively affects the oxygen release behavior at high temperatures.

Why Cobalt-free material?

- Insufficient supply
- Rising cost
- Moral issues

Why particle morphology design?

- To minimize the use of Cobalt
- To get the advantage of cobalt on the surface or inside the particle

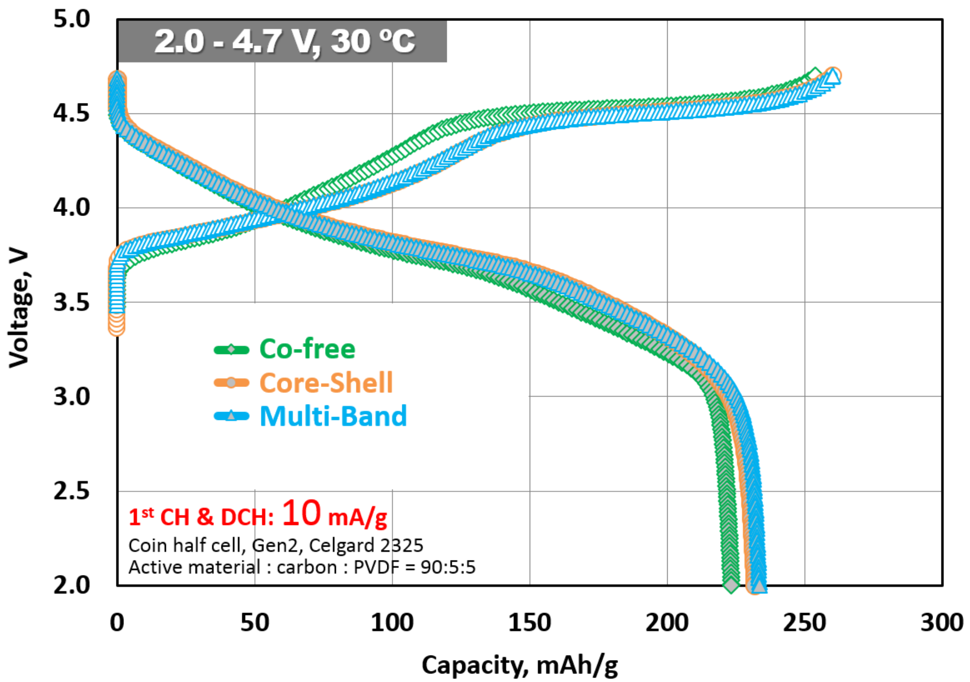


Preliminary synthesis study

Core composition : Co-free material

$0.34Li_2MnO_3 \bullet 0.66LiNi_{0.5}Mn_{0.5}O_2$

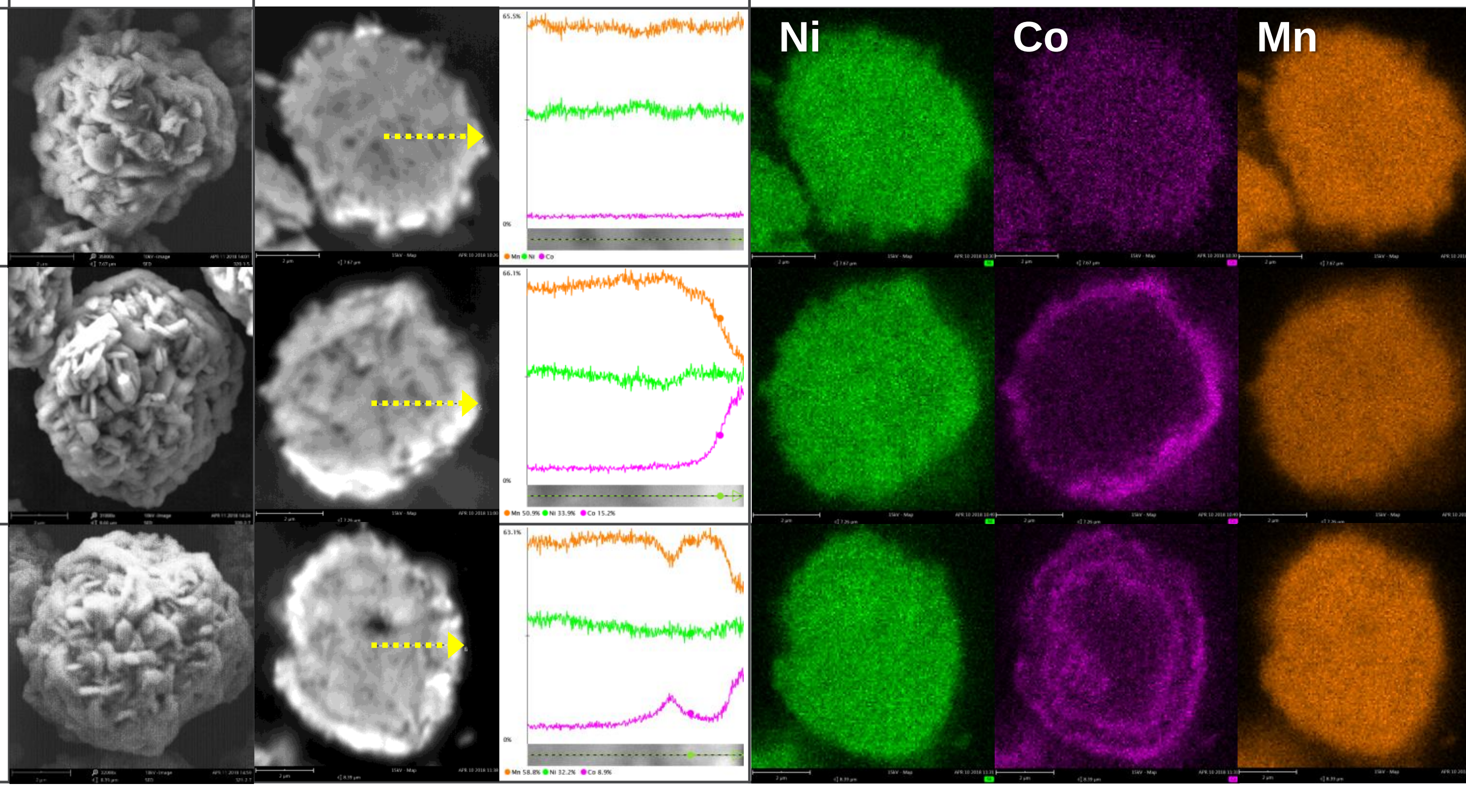
Shell & Band composition : NMC 333



Cobalt-free Lithium-manganese-rich Material

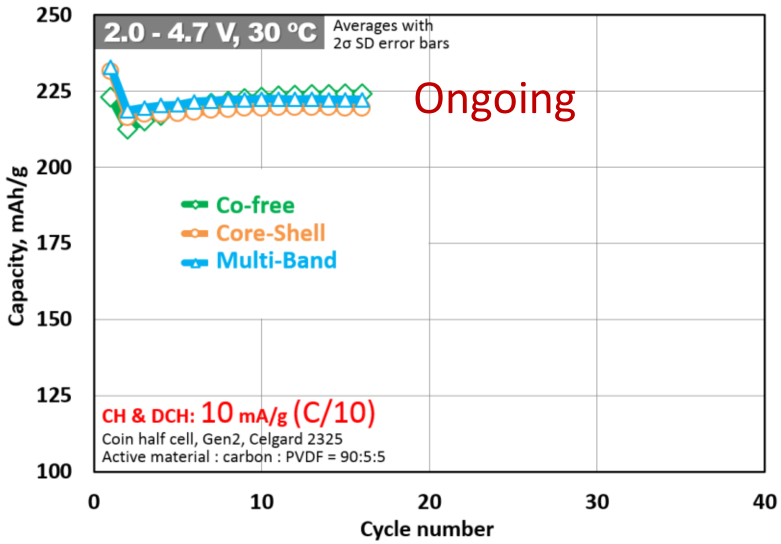
- Preliminary synthesized Co-free, Core-Shell and Multi-Band materials

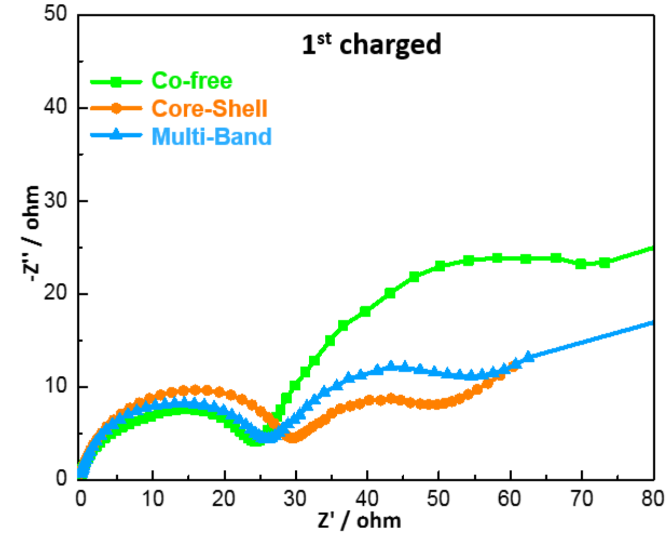
Particle design	SEM	Cross-sectional line scan	Cross-sectional mapping
Co 0% Cobalt-free ICP: $Li_{1.39}Ni_{0.32}Co_{0.00}Mn_{0.68}O_2$			
Co 9% Core-Shell ICP: $Li_{1.29}Ni_{0.31}Co_{0.09}Mn_{0.60}O_2$			
Co 8% Multi-Band ICP: $Li_{1.30}Ni_{0.31}Co_{0.08}Mn_{0.61}O_2$			

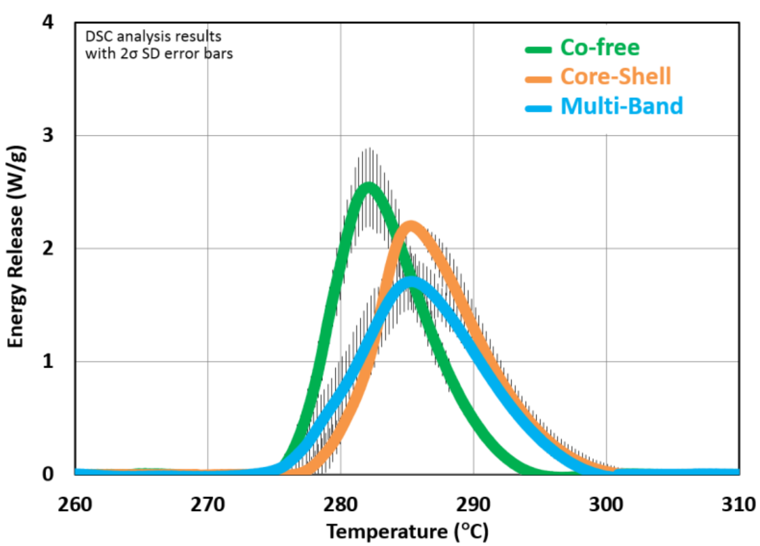


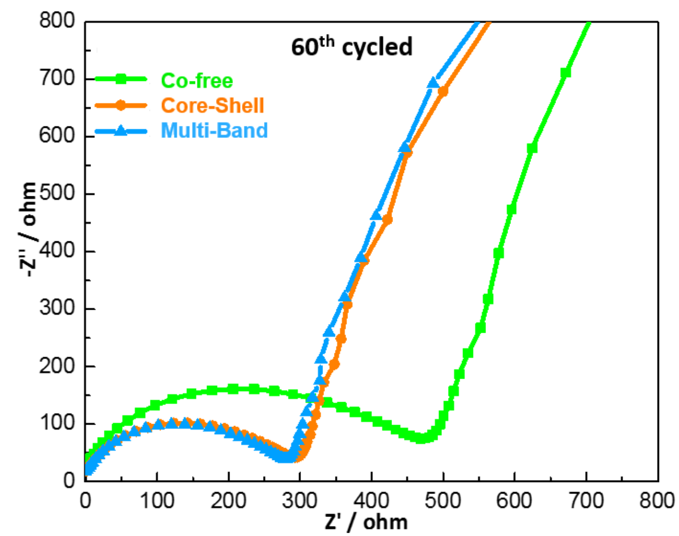
✓ *The particle structure composed of Co-free material and NMC333 shows the possibility of a positive physical combination of Co-free material and other heterogeneous materials.*

Cobalt-free Lithium-manganese-rich Material









✓ *Core-Shell and Multi-Band structures shows the possibility to use Cobalt at a minimum and to maximize its effect.*

Responses to Previous Year Reviewers' Comments

- "The reviewer remarked that progress is excellent, but suggested that more consideration of crystal homogeneity in the materials produced needs to be demonstrated."
  - *Response: We are collaborating on X-ray absorption spectroscopy analysis to closely examine the crystallinity of the interior and surface of the synthesized gradient materials. In particular, the interfacial properties of heterogeneous materials are one of the major concerns.*

- "They showed better rate capability and limited cycling performance in half cells using their 811 core gradient material. However, they ultimately need to validate the performance advantage of the 811 core gradient material in a full cell."
  - *Response: We are evaluating pouch full cell in early stage for selected 4 kinds of gradient materials. A systematic full cell assessment will be performed on gradient materials produced in kilograms in the future.*

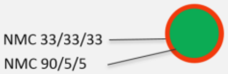
- "The reviewer commented that progress toward actually making a core gradient material that cycles well is good, but it is not clear what the fading mechanism is. It is important to do some diagnostic tests, such as impedance measurements to seek the reasons."
  - *Response: Impedance measurement was carried out to understand the aspect of the fading. In addition, we will attempt to identify surface changes by analyzing the surface structure of the material that has undergone long-term cycle.*

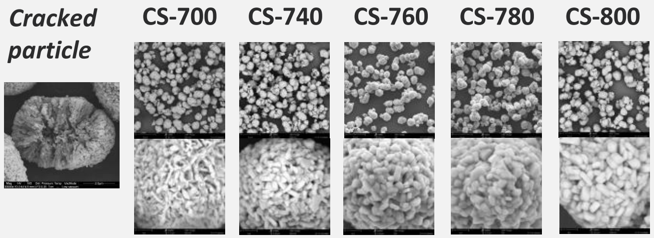
Collaborations

Prof. Sangkee Min

- Nano indentation:
  Particle strength analysis

Delivered materials:
Five 811 Core-Shell materials





CSE CAMP

- Coin full cell evaluation
- Pouch cell evaluation

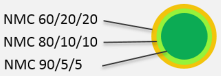
Delivered materials:

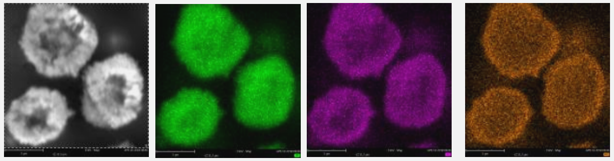
100 gram 811 Core-Shell
100 gram 811 Core-Gradient
100 gram Core-Multi Shell 811
100 gram Core-Multi Shell 622

Dr. Feng Wang

- FIB for electron microscopy
- XANES and EXAFS

Delivered material:
811 Core-Shell
Core-Multi Shell 811

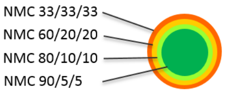


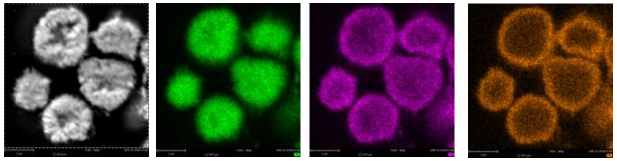


Dr. Sungmin Park

- Hard X-ray Nanoprobe imaging
- XANES and EXAFS
- Thermal stability studies

Delivered material:
Core-Multi Shell 622





CEO Jongpal Hong

- Equipment manufacturing
- Development and scale-up of advanced synthesis technology

Taylor Vortex Reactors

Remaining Challenges and Barriers

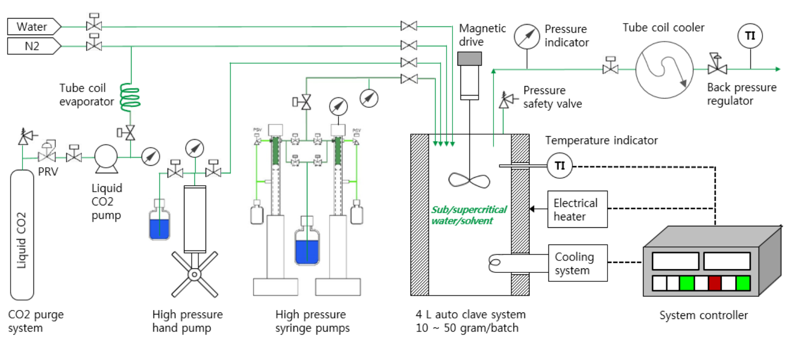
- Development and scale-up of concentrated gradient cathode material is challenging but has great promise to improve the performance of battery materials.

- Continuous synthesis process for concentrated gradient cathode material need to be developed to lower manufacturing cost.

- Synthesis of Co-free gradient materials with minimal cobalt content is not easy, but systematic studies are required to improve the performance of Co-free materials.

Proposed Future Research

- Further refinement of NMC gradient material
  - Kg production of a NMC gradient material based on CAMP pouch cell result
  - Investigate new particle structure and composition combination
  - Development of continuous synthesis process of gradient material
- Cobalt-free lithium-manganese-rich material
  - Synthesis research on Cobalt-free lithium-manganese-rich materials
  - Cobalt-free Gradient material (Core-Shell, Multi-Shell, Multi-Band, …)
  - Kg production of Cobalt-free material for the baseline of fundamental research
- Hydro/solvothermal synthesis of nano-size single-crystal active battery material
  - Systematic synthesis research on nano-size highly-crystalline active battery materials (ex. Co-free)
  - Nano-level surface modification on scaled active battery materials



Any proposed future work is subject to change based on funding levels.

Summary

- **622 & 811 Core- Gradient material characterizations**
  - Hard X-ray nanoprobe imaging
  - Thermal stability studies

- **Synthesis and evaluation of Core-Multi Shell materials**
  - NMC90/5/5
  - Core-Multi Shell NMC90/5/5 + 811
  - Core-Multi Shell 811 (NMC90/5/5 + 811 + 622)
  - Core-Multi Shell 622 (NMC90/5/5 + 811 + 622 + 333)

- **Early stage pouch cell evaluation**
  - 100 gram 811 Core-Shell
  - 100 gram 811 Core-Gradient
  - 100 gram Core-Multi Shell 811
  - 100 gram Core-Multi Shell 622

- **Preliminary synthesis of Cobalt-free lithium-manganese-rich material**
  - Co-free high energy material ($0.34Li_2MnO_3 \bullet 0.66LiNi_{0.5}Mn_{0.5}O_2$)
  - Core-Shell particle structure (Co-free + NMC333)
  - Multi-Band particle structure (Co-free + NMC333)

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